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14. ABSTRACT

Composite materials are critical for many engineering applications because of the resultant properties that arise from the combination of dissimilar constituent materials. A particularly exciting class of constituent materials is shape memory alloys (SMAs), which continue to be explored because of their unique superelastic capabilities. This research effort was focused on developing methods to synthesize SMA composite structures, characterizing shape memory composites, and creating materials suitable for use in miniaturized components and structures. A range of topics was explored under this topic area. Accomplishments and new findings included the fabrication of NiTi shape memory nanoparticles using a rolling and folding technique, the development of a new technique for manipulating and controlling the motion of individual nanoparticles using magnetic fields, and the demonstration of improved mechanical adhesion between NiTi and a polymeric matrix using chemical functionalization.

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Nanostructured Shape Memory Alloys:
Composite Materials with Shape Memory Alloy Constituents

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March 2004

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Contents

Executive Summary

Composite materials are critical for many engineering applications because of the resultant properties that arise from the combination of dissimilar constituent materials. A particularly exciting class of constituent materials is shape memory alloys (SMAs), which continue to be explored because of their unique superelastic capabilities. These alloys already have wide ranging applications in the aerospace, biomedical, and microelectronics industries. For example, control of flight using SMAs has been demonstrated with microelectromechanical systems (MEMS) to change the fluid dynamics on a wing. Miniature aeronautic vehicles have also been conceived that utilize SMAs and other active materials in a number of different functions. As the dimensions of these devices become smaller and the demands on their performance grow, the need for materials that function optimally in these environments becomes critical. Combining the properties of SMAs with other materials in composite structures will create opportunities for making multifunctional components and components capable of performing in ways that surpass the constituent materials.

The objective of this research effort is to improve the application of shape memory alloys (SMAs) to microscopic structures and miniaturized devices by:

1) developing methods to synthesize SMA composite structures;
2) characterizing shape memory composites; and
3) creating materials suitable for use in miniaturized components and structures.

Our AFOSR-funded research explored synthetic methods for the production of shape memory particles and nanowire structures using chemical and electrochemical deposition techniques. Core-shell nanoparticles were produced by chemical reduction and segmented nanowires were created with electrochemical deposition. These constituent materials were produced for use in composite materials and structures. Our research demonstrated that manipulation of individual liberated nanowires can be accomplished by both electrical and magnetic fields which is useful for the construction of nanoscale devices. In addition, functionalization techniques were explored to customize the interface between the shape memory alloy and the composite matrix in which it may be employed. All of the materials created in this effort were rigorously characterized to identify size, composition, and crystallographic structure.

Accomplishments and new findings included:

- Fabricated shape memory nanoparticles of NiTi using a rolling and folding technique.
- Developed nanoparticle co-synthesis and core-shell synthesis techniques for nanobronze systems that are related to the CuSn shape memory alloy phase.
- Produced bristled structures composed of nanowires on a substrate and individual liberated nanowires using electrodeposition in nanoporous membranes.
- Manipulated and controlled the motion of individual liberated nanowires using nickel end caps and magnetic fields.
- Investigated nanoscale martensitic structures in NiTi by transmission electron microscopy and observed a new interwoven martensite/austenite structure.
- Developed a functionalization strategy for improving adhesion between a shape memory alloy constituent in a polymeric matrix.

Personnel supported by this research effort:

Wendy C. Crone, Assistant Professor, Engineering Physics
Arthur B. Ellis, Professor, Chemistry [currently on detail at the National Science Foundation]
John H. Perepezko, Professor, Materials Science and Engineering

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Nick Smith, Graduate Research Assistant, Chemistry (Ph.D. expected December, 2004)

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Publications included four refereed journal papers (submitted, in press, and published), one thesis, and an article in a on-line trade journal:

N.A. Smith, N. Sekido, J.H. Perepezko, A.B. Ellis, W.C. Crone, "Synthesis of Dual Phase Bronze Alloys
    from Elemental Nanoparticle Constituents," submitted to *Scripta Materialia.*
N.A. Smith, G. Antoun, A.B. Ellis, W.C. Crone, "Improved adhesion between a NiTi SMA wire and a
    polymer matrix via silane coupling agents," to appear in *Composites A.*
A.K. Bentley, J.S. Trethewey, A.B. Ellis, W.C. Crone, "Magnetic Manipulation of Copper-Tin Nanowires
    Capped with Nickel Ends," *Nano Letters,* 4(3) 487-490 (2004).
L. Tan and W.C. Crone, "In situ TEM observation of two-stage martensitic transformation in aged NiTi
    shape memory alloy," *Scripta Materialia,* 50(6), pp.819-823 (2004).

G.G. Antoun, "Improving the Adhesion Between a NiTi Wire and Polymer Matrix for Composite
    Applications – and – Mechanical Fabrication of Nanometer-Sized Shape Memory Alloy Niti
    Particles from Bulk by Rolling and Folding," Thesis, Masters of Science in Engineering
    Mechanics, University of Wisconsin – Madison, Madison, WI (2003).

"Nickel nanowire caps lead to manipulation," by Liz Kalaugher, nanotechweb.org, February 3,
    2004, http://nanotechweb.org/articles/news/3/2/1/1

Introduction

Composite materials are critical for many engineering applications because of the resultant properties that arise from the combination of dissimilar constituent materials. A particularly exciting class of constituent materials is shape memory alloys (SMAs), which continue to be explored because of their unique superelastic capabilities. This research effort was focused on developing methods to synthesize SMA composite structures, characterizing shape memory composites, and creating materials suitable for use in miniaturized components and structures. A range of topics was explored under this topic area. Accomplishments and new findings included the fabrication of NiTi shape memory nanoparticles using a rolling and folding technique, the development of a new technique for manipulating and controlling the motion of individual nanoparticles using magnetic fields, and the demonstration of improved mechanical adhesion between NiTi and a polymeric matrix using chemical functionalization.

Nanoparticle Synthesis

To take advantage of the improvements that can be realized due to size effects of the composite inclusions, research efforts have emerged to find methods to create nano-sized SMA particles. However, the difficulty of creating nano-SMA is evidenced by the scarcity of fabrication methods currently available in the literature. We explored several synthesis and fabrication routes for the production of shape memory nanoparticles. There are numerous alloy systems that exhibit shape memory properties. The most widely known and commercially viable alloy is NiTi. In addition to NiTi, we also explored CuSn alloys; Cu and Sn are more amenable to chemical reduction techniques.

Mechanical Fabrication of Nanoparticles

> G.G. Antoun, "Improving the Adhesion Between a NiTi Wire and Polymer Matrix for Composite Applications – and – Mechanical Fabrication of Nanometer-Sized Shape Memory Alloy Niti Particles from Bulk by Rolling and Folding," Thesis, Masters of Science in Engineering Mechanics, University of Wisconsin – Madison, Madison, WI (2003).

There are few fabrication techniques for nano-sized NiTi shape memory alloy particles. We developed a new mechanical fabrication technique in an effort to produce shape memory particles for characterization and composite fabrication purposes. We used a method previously developed by co-PI Dr. John Perepezko for more conventional metals, to produce NiTi shape memory particles with a range of particle sizes down to the nanometer regime. Progressive cold rolling of thin shape memory alloy strips sandwiched between sheets of polypropylene was conducted to exploit the instability that forms at the interface between the polymer and the alloy to break up the NiTi into a wide distribution of particle sizes.

This new method for creating nano-sized shape memory particles can be applied with very little time investment, resources, or specialized equipment. The breakup of the NiTi is shown at three different stages in Figure 1. SEM observations have shown that the fracturing process creates a wide distribution of nano-sized particles. DSC studies on the remaining bulk (~1mm) particles have shown that mechanically deformed NiTi reduces the martensite-to-austenite transformation characteristics, which is in accord with previously reported studies. Limited TEM observations of the nano-sized particles have shown that the rolling process induces amorphization and the appearance of a variety of atomic structures, including austenite. It is intriguing that the TEM results showed that none of the structures underwent a thermally induced phase transformation over the temperature range −120°C to

40°C. This may be due to "pinning" of austenite by lattice defects or due to transformation temperatures shifts at the nanoscale.
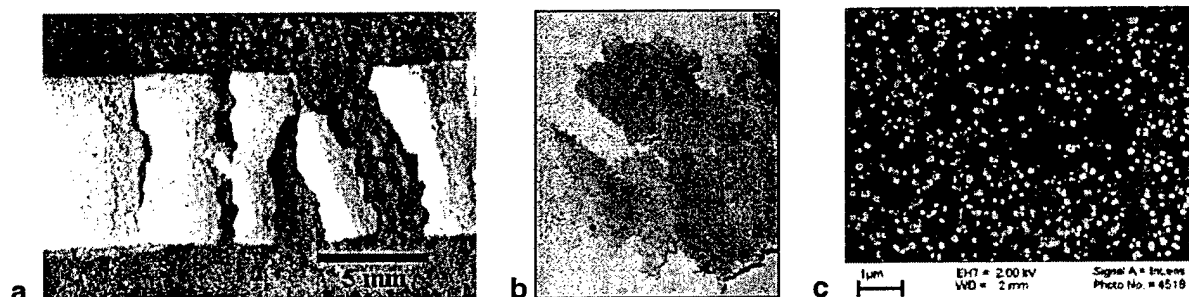
Figure 1. a) NiTi/PP composite after 1mm mandrel separation pass of first cycle showing fracture of NiTi perpendicular to rolling direction. b) NiTi/PP composite after 5 cycles with a range of particle sizes. Image is 6 cm X 6.5 cm. c) SEM image of sub-micron NiTi particles liberated from the NiTi/PP composite after 5 cycles.

Chemical Synthesis of Nanoparticles

N.A. Smith, N. Sekido, J.H. Perepezko, A.B. Ellis, W.C. Crone, "Synthesis of Dual Phase Bronze Alloys from Elemental Nanoparticle Constituents," submitted to *Scripta Materialia*.

Alloys such as bronzes have played a major role in the customization of bulk materials and may be expected to provide similar opportunities for tuning the properties of nanoscale materials. Recently, Wolfenstein et al. synthesized the η phase of copper-tin, η-$Cu_{0.55}Sn_{0.45}$, for a rechargeable battery application [1]. Their synthesis involved co-reduction with borohydride of divalent Cu and Sn salts. We demonstrate that sequential reduction of these salts can lead selectively and in high yield to nanoparticles of β-CuSn (13.5 at% Sn).

We have shown that phases that are not stable at room temperature can still be achieved by more conventionally quenching methods while maintaining nanoscale grain structures. In a typical synthesis of the nanoparticles, Sn(II) solution was added via syringe to a solution of excess borohydride with stirring. The solution became slightly yellow upon initial addition, then turned grey and opaque over the 20 seconds during which the stannous solution was added. At this point, Cu(II) solution was added by syringe, forming an agglomerated black precipitate. The resulting particle sizes for tin and copper were estimated to be 90-120 nm and 10-30 nm, respectively prior to heat treatment. The dried material was cold-worked by passing it once through a rolling mill to consolidate the heterogeneous mixture of nanoparticles. The cold-worked substance was then placed in a sealed tantalum foil envelope, and heated to 700°C for ca. 2 minutes. It was then quenched rapidly by immersion into an ice bath. After this treatment, the material exhibited a yellowish color typical of a bronze.

Powder XRD patterns, SEM images and TEM examination were used to determine the phase identity and compositions in the samples during various stages of the synthesis. The particle sizes for tin and copper were estimated to be 90-120 nm and 10-30 nm, respectively, over a range of samples. The TEM image of the same material in Figure 1a confirms the size estimate and reveals that the elemental nanoparticles are arranged into aggregates with sizes of the order of hundreds of nm. Different areas of the sample that were analyzed by electron diffraction, which indicated that the larger, darker features

in Figure 1a are tin, and the smaller aggregates are copper. Evidently there was an effective mixing of the component aggregates.

The effectiveness of the consolidation is illustrated in Figure 1b that is a backscattered electron image of the cold-worked material prior to annealing. Following consolidation by cold rolling, the mixed aggregate array exhibited some larger scale agglomeration and yielded a few elongated micron size Sn regions as well as the finer as-synthesized Sn aggregates that were fairly well dispersed within the Cu matrix. The α and β phase compositions are close to the values expected for the tie line end points in the ($\alpha + \beta$) two-phase field at 700°C. Complete reaction of the elemental components has occurred to yield an overall alloy composition in the two-phase ($\alpha + \beta$) region.
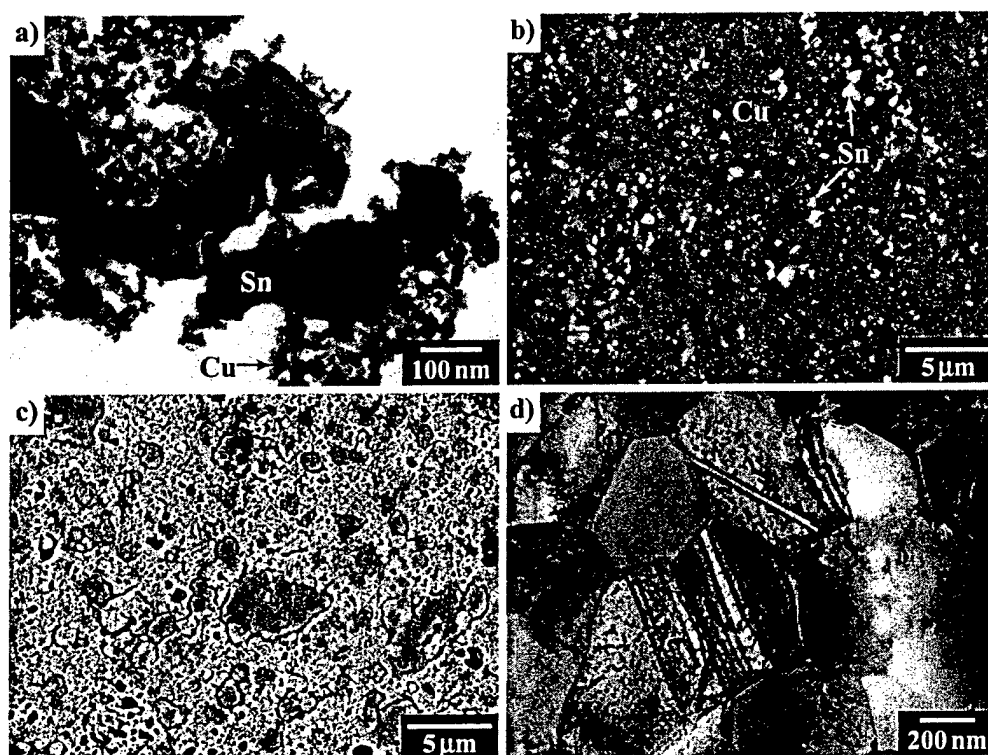
Figure 1. a) Bright field image of the precipitated, dried product, b) backscattered electron image of as-rolled material, c) backscattered electron image of the annealed material, d) bright field image of the annealed material.

Figure 1c, a backscattered electron image of the annealed material, reveals the two-phase microstructure. A closer inspection of the microstructural morphology that is evidenced in Figure 1c demonstrates that the apparent Cu-rich and Sn-rich regions that are indicated by the back-scattered imaging do not represent the actual two-phase microstructure. Instead, higher resolution TEM reveals that each region in Figure 1c is actually a two-phase mixture of the α and β phases; a representative TEM micrograph is shown in Figure 1d. In other words, there is a duplex morphology of two-phase regions consisting of a Cu-rich ($\alpha + \beta$) region and a Sn-rich ($\alpha + \beta$) region. Moreover, the size scale of the duplex morphology is comparable to that for the Sn-rich and Cu-rich regions in the consolidated, un-reacted sample (Figure 1a). The reacted sample has the appearance of a well annealed microstructure structure with a well dispersed two phase array. There is no clear indication of transformation of the β phase. Since the β phase for a Cu-14 at.%Sn composition in bulk samples has been reported to form martensite products upon quenching to room temperature [2], the stabilization of

the β phase in the present work is an intriguing result. Further, the α phase grains also reveal annealing twins that is again characteristic of an equilibrated microstructure. However, on the larger scale of the image area in Figure 1c, the microstructure is represented by a mixture of two–phase regions with different compositions and different relative phase fractions.

Two-phase (α + β) bronze alloys with sub-micron grains can be obtained through a relatively simple synthetic diffusional reaction scheme, however no shape memory behavior was exhibited. The product microstructure has a novel duplex morphology of dual phase regions consisting of a Cu-rich (α + β) region and a Sn-rich (α + β) region. We have shown that phases that are not stable at room temperature can still be obtained by more conventional quenching methods while restricting grain growth.

Nanowire Synthesis

Recently, techniques have been developed to allow the production of nanoscale wires and rods using nanoporous alumina or polycarbonate filtration membranes as templates. Martin and colleagues first developed the template synthesis method in the late 1980s [3]. In this technique, a membrane's pores are filled with one or more metals via a technique such as electrodeposition. The membrane can be chemically removed, leaving metallic nanowires behind [4]. The diameter of the nanowires corresponds to the original diameter of the membrane template, and the length of the wires can be as long as the original template is thick. Most porous templates are made from anodized aluminum or track-etched polycarbonate and have diameters ranging from 200nm to 20nm. Since the initial development of the template technique, researchers worldwide have successfully adapted it to synthesize nanoscale semiconductors, semiconductor oxides, superconductors, magnetic structures, polymers, and giant magnetoresistance (GMR) materials [5-9]. It is hypothesized that nanowires will be used to increase magnetic recording densities, to build nanocircuits and nanoelectromechanical machines, and to sense single molecules. It is impractical to electrodeposit NiTi nanowires, as Ti^{4+} is quite difficult to reduce electrochemically. However, there is a group of Cu-based shape memory alloys, some of which can be electrodeposited. Of these CuSn is most feasible, as it is deposited from acidic sulfate deposition baths.

Electrodeposition can be used to create binary alloys, usually with both metals dissolved as salts in the same deposition bath. The pulse electrodeposition technique illustrated in Figure 1 is well-suited to depositing binary (and ternary) alloys. In this method, the applied potential is varied between a potential that is sufficiently negative to reduce metal A (the metal with the more positive reduction potential) but not negative enough to reduce metal B. At this point only metal A deposits at the cathode. Then the potential is switched to a more negative value, where both metal A and metal B are deposited. To avoid depositing too much metal A in the metal B layer, the overall concentration of metal A in solution is kept very low. If the metals are deposited in layers that are sufficiently thin, the two metals will interdiffuse to form an alloy at room temperature. Electrochemical deposition parameters such as solution composition, deposition potential, and pulse length will be varied to achieve the ratio of 85% Cu to 15% Sn corresponding to the bulk shape memory composition. Once the pores are filled with the two metals in the target ratio, the phase with the shape memory effect can be formed by heating the rods to 750 °C (determined from the CuSn phase diagram) and then quickly submerging them into liquid nitrogen in an attempt to obtain the desired phase. We explored this technique extensively with the CuSn system, but the shape memory property was never observed. We speculate that the nanometer scale particle size and the highly refined nanometer grain size inhibited formation of the appropriate phase.
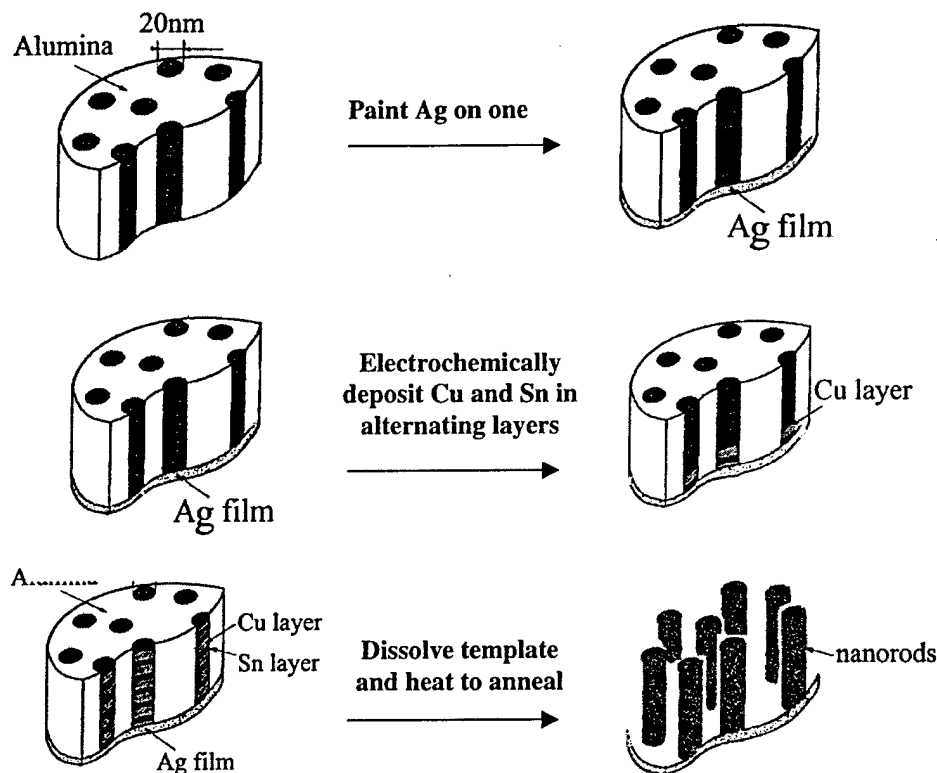
Figure 1: *Schematic diagram of the electrodeposition of nanowires in an alumina membrane.*

Using this basic synthetic strategy, we have produced nanoscale bristled structures. The alumina membrane template can be easily dissolved using a strong base, leaving an array of metallic nanowires attached to a substrate. Leaving the conductive layer intact has allowed us to produce a brush-like structure shown in Figure 2. In these images we have shown a section of the structure near a bend in the substrate so that the aspect ratio of the nanowires can be seen. The bristles are approximately 5000 nm in length and 200 nm in diameter, corresponding to an aspect ratio of 25:1. We explored the use of these bristled structures in microfluidic devices for passive mixing control with some moderate success.

To completely liberate the rods from both the alumina and the silver, first the silver backing was dissolved with 10 M HNO_3. After the sample was rinsed with deionized water, a basic solution was used to dissolve the alumina membrane and the rods became suspended in the solution. The polymer support (which was freed from the membrane) was removed with tweezers and discarded. The solution of nanowires was transferred to a test tube and centrifuged. The strongly basic solution was decanted, and the rods were re-suspended in the desired solvent.

After the rods are liberated from the silver backing and the alumina membrane, they can be seen using an optical microscope. The density of nanowires on the microscope slide can be controlled by varying the concentration of nanowires in solution. Figure 3 shows typical optical microscope images of the rods and demonstrates the variation in nanowire concentration. A number of experiments explored the manipulation of these liberated nanowires.
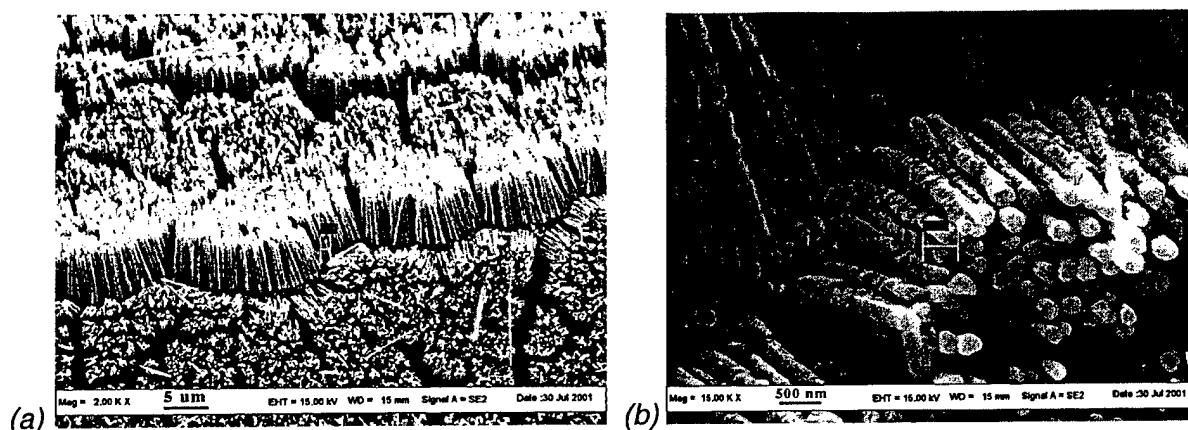
Figure 2. a) *Nanoscale rods of copper attached to a silver substrate. The nanoscale bristled structure contains thousands of bristles, each with an aspect ratio of approximately 25. b) An enlarged view of the nanowires. Both images show a section of the structure near a bend in the substrate.*
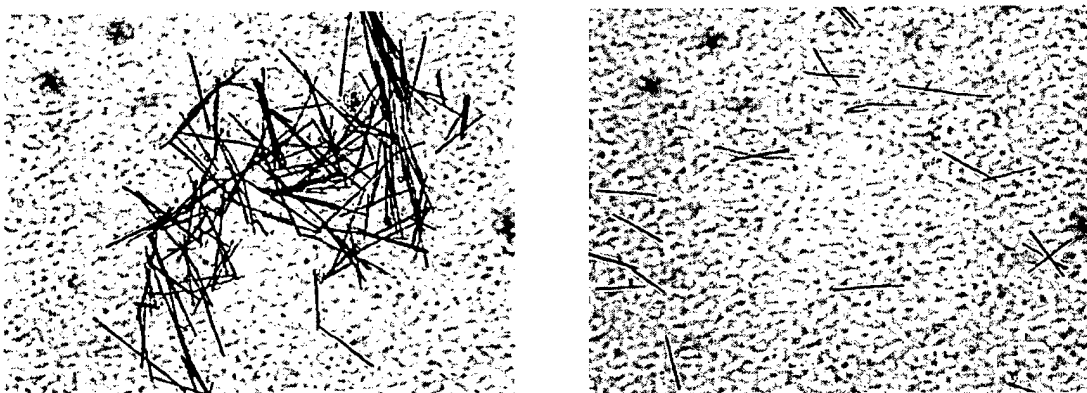
Figure 3. *CuSn nanowires dispersed in water as seen at 50X. The image on the left is a drop with a higher concentration of nanowires. The nanowires are approximately 20 μm long.*

Manipulation and Control of Individual Nanowires

A.K. Bentley, J.S. Trethewey, A.B. Ellis, W.C. Crone, "Magnetic Manipulation of Copper-Tin Nanowires Capped with Nickel Ends," *Nano Letters*, 4(3) 487-490 (2004).

"Nickel nanowire caps lead to manipulation," by Liz Kalaugher, nanotechweb.org, February 3, 2004, http://nanotechweb.org/articles/news/3/2/1/1

To measure the properties of nanowires and eventually incorporate them into devices, it is essential to be able to control their movement and position. A number of research efforts have examined this problem. In surfactant solutions, gold nanowires will self-assemble into close-packed monolayers on surfaces [10]. Others have controlled the movement and alignment by utilizing the wires' response to electric fields. Precise alignment of gold nanowires between Ti/Au electrodes was achieved by using an alternating nonuniform electric field [11]. This was due to the polarization of individual nanowires so that each is attracted toward the strongest field - the area close to the electrode. Because the field is alternating, the nanowires are alternately attracted to each electrode and are thus immobilized and

aligned between the two electrodes. Very recently, reports have surfaced of using magnetic fields to align nanowires. Ni nanowires prepared using alumina membranes were liberated from the template and suspended in a solvent. When a magnetic field was applied across the solution, the nanowires aligned parallel to the magnetic field lines [12].

We explored the manipulation and position control of metallic nanowires under magnetic fields. The rods are first liberated from both the alumina membrane and the silver backing, rinsed with deionized water, and centrifuged. The rods were re-suspended in the desired solvent. We demonstrated the ability to control ANY conductive nanowire with a magnetic field. This is accomplished by electrodeposition of one or two Ni end caps on wire during the growth process.

In order to explore magnetic control of the nanowires, a Ni end of 2 μm was deposited onto the CuSn nanowires of approximately 15 μm in length.The wires with magnetic ends were suspended in solvent, dropped on glass microscope slides, and then covered with a cover slip. These wires moved in response to a magnet. When a single bar magnet is held to the side of the vial containing Ni-CuSn or Ni-CuSn-Ni wires in solution, the black nanowires all move toward it and aggregate next to the magnet in less than 5 seconds. Similarly, when a magnet is held at one side of a drop of these Ni-containing wires on a microscope slide, they move toward the magnet. This can be seen both with the naked eye – an agglomeration of nanowires appears black or grey – or with the optical microscope. This property was utilized to align the nanowires using two bar magnets, as shown in Figure 1. When the two magnets are attracting each other, the nanowires align horizontally; when the magnets repel, the nanowires align vertically. The rods are aligning parallel to the magnetic field lines between the two magnets in each case. When one magnet is held in front of the sample and rotated, the magnetic nanowires spin on the slide much like a magnetic stir bar does. We also explorered incorporation of this "nano stirbar" concept into a microfluidic device.

The ultimate goal of our research is to be able to control the movement and alignment of nanowires for their use in structures and the ability to measure their properties. Our current method for this is shown in Figure 2. Nickel pads are deposited on a substrate and magnetized. The pads are then exposed to a solution containing nanowires with Ni end caps. Upon drying of the solution the rods are observed to bridge the gap between the pads. Once a nanowire is positioned over a trench, we can use a scanning probe technique to image the wires.

The success of this technique provides an additional tool for the construction of nanoscale devices. This is an exciting new method for manipulation of nanowires because it is so versatile. By creating nickel end caps on a nanowire during its synthesis, you later have the ability to control the wire's orientation with a magnetic field. The options are quite broad for the material deposited between the nickel.

Figure 1. *Sequential optical microscope images of Ni-CuSn-Ni nanowires suspended in ethylene glycol as they are spun clockwise using a rotating magnetic field. The scale bar shown in frame (a) is 50 μm.*
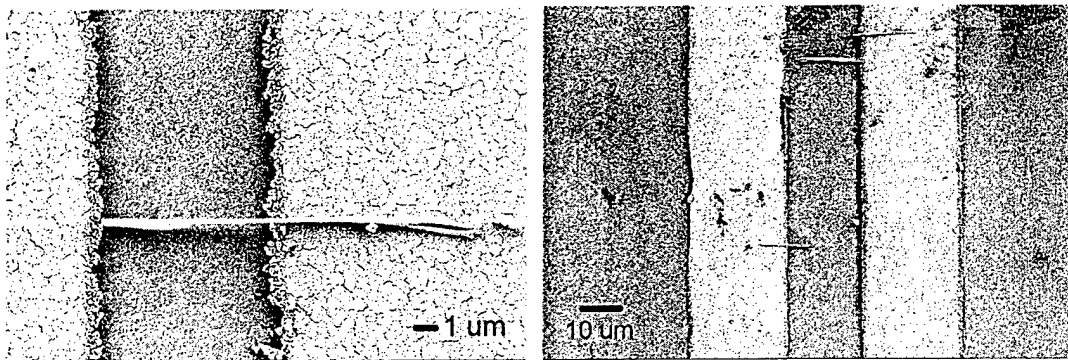
Figure 2. SEM image of a Ni-CuSn-Ni nanowire aligned between two nickel stripes (lighter color) on silicon (darker color).

Nanoscale Martensite Structures

L. Tan and W.C. Crone, "In situ TEM observation of two-stage martensitic transformation in aged NiTi shape memory alloy," *Scripta Materialia*, 50(6), pp.819-823 (2004).

As discussed above, the nanosize scale can have an impact on a material's ability to undergo the solid-solid phase transformation observed in shape memory alloys. In order to better understand this phenomenon, the martensitic transformation was investigated in an aged NiTi alloy with a temperature controllable TEM specimen stage.

Using TEM at room temperature, the material was shown to be in the austenite phase with selected area diffraction (SAD). The two-step transformation (austenite to R-phase then martensite) observed by DSC was verified by TEM upon cooling with liquid nitrogen. At low flux of liquid nitrogen in the TEM specimen stage, R-phase formed first generating a stress field which reduced the phase transformation barrier of martensite. As shown in Figure 1, the parallel structure of the R-phase grows from the nucleus sites at the surface boundaries of the $Ti_{11}Ni_{14}$ precipitates, which is in accordance with the findings of Kainuma *et al.* [13]. The $Ti_{11}Ni_{14}$ phase can introduce internal tensile stress originating from the different density between the $Ti_{11}Ni_{14}$ and matrix (B2) and the misfit strain [14]. The stress state created by the presence of these precipitates decreases the barrier to R-phase transformation and the martensitic transformation that follows. The restriction of the $Ti_{11}Ni_{14}$ precipitates on the growth of the R-phase is also indicated in Figure 1, which confirms the suggestion that the high density of $Ti_{11}Ni_{14}$ precipitates in the matrix of the aged Ni-rich NiTi SMAs are related to the smaller R-phase domain [15]. A martensite phase domain forming in a region of R-phase is shown in the upper left corner of Figure 1. Martensite does not appear around the $Ti_{11}Ni_{14}$ precipitates due to the larger nucleation barrier to martensite compared to that with R-phase [16].

At high flux of liquid nitrogen in the TEM specimen stage, an interwoven austenite/martensite structure originates at the boundary of the R-phase and parent phase and grows into both the parent phase and the R-phase regions. The R-phase fraction diminished with the growth of the martensite, which may support the argument of Dlouhy *et al.* [17] that the R-phase transforms to B19' in addition to the direct transformation from B2 to B19'. An interwoven austenite/martensite structure, shown in Figure 4, with white cells denoting the austenite phase and black and gray cells denoting the martensite variants was stabilized at this lower temperature. The corresponding diffraction pattern of Figure 2 with zone axis [111]$_{B2}$ is shown in the inset. The large bright diffraction spots forming an equilateral triangle result

from the austenite phase; and the streaks beside the austenite diffraction spots result thin lamellae of the martensite variants. The dim diffraction spots in a hexagonal pattern surrounding the large austenite diffraction spots correspond to the R-phase in the up-right corner of the bright-field image (Figure 2).

This is the first time that this type of interwoven austenite/martensite structure has been reported to be observed in NiTi. In contrast to the situation in bulk shape memory alloys where it is not possible to form an interface between austenite and a single variant of martensite, in thin films the situation can be quite different [18]. A similar interwoven austenite/martensite structure to that observed experimentally was predicted analytically for CuAlZn SMAs by Sreekala et al. with a two-dimensional model [19]. According to the in situ TEM observations shown here, this interwoven structure forms preferentially in defect-free and precipitate-free regions which are surrounded by the R-phase in the thin planar TEM sample. The formation of the interwoven austenite/martensite structure is thought to be a result of the strains surrounding the R-phase, which favor the growth of the slabs along the certain directions [19].

These results may give some insight into the inhibition of phase transformation observed in nanoscale shape memory alloys. The high surface area to volume created by nanostructuring constrains and highly influences the structures formed.
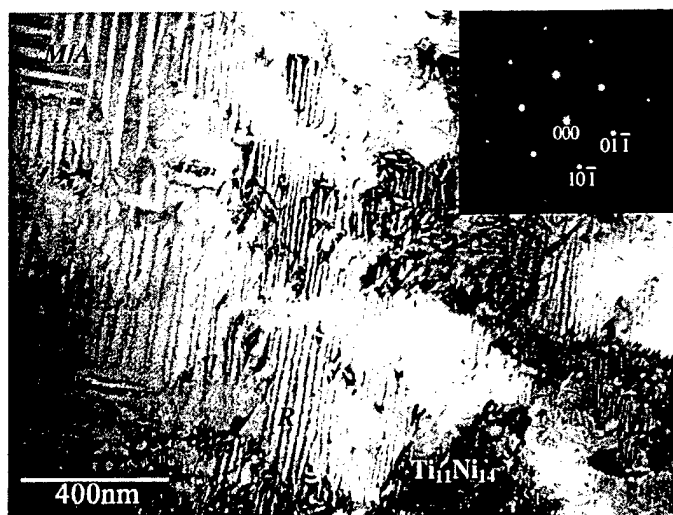
Figure 1. Bright-field image of the aged Ni-rich NiTi SMA demonstrating the correlation of $Ti_{11}Ni_{14}$ precipitates, R-phase (R), and interwoven austenite/martensite (M/A) phases. The inset is the select area diffraction pattern taken at the region labelled M/A prior to cooling, which indicates the parent phase was austenite with $[111]_{B2}$ zone.
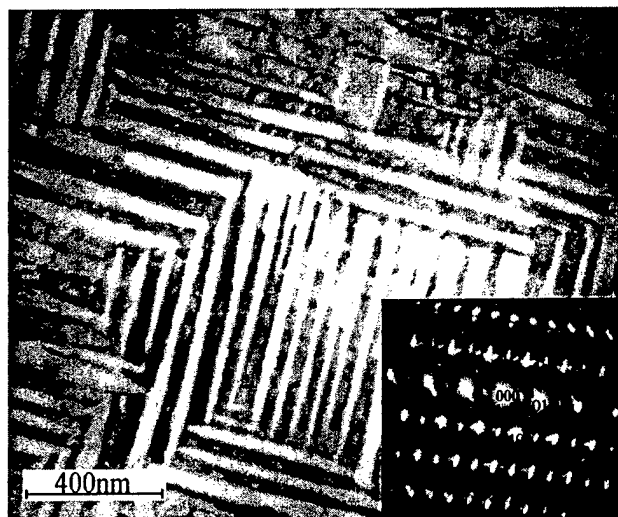
Figure 2. Bright-field image of martensitic bands in 50nm width. White cells correspond to the austenite phase and black and gray to the martensite variants. The diffraction pattern with the zone axis $[111]_{B2}$ corresponds to the bright-field image, where the large bright diffraction spots in equilateral triangle correspond to austenite phase, and the small diffraction spots beside the diffraction spots of austenite phase correspond to the martensite phase.

Adhesion of SMA Materials to a Polymeric Matrix

N.A. Smith, G. Antoun, A.B. Ellis, W.C. Crone, "Improved adhesion between a NiTi SMA wire and a polymer matrix via silane coupling agents," to appear in Composites A.

G.G. Antoun, "Improving the Adhesion Between a NiTi Wire and Polymer Matrix for Composite Applications – and – Mechanical Fabrication of Nanometer-Sized Shape Memory Alloy Niti Particles from Bulk by Rolling and Folding," Thesis, Masters of Science in Engineering Mechanics, University of Wisconsin – Madison, Madison, WI (2003).

Following widespread commercial application of shape memory alloys such as NiTi, reports of active composite materials involving a shape memory alloy constituent began to appear in the mid 1990s. Commonly NiTi wires, ribbon, or particles are embedded in a polymer matrix to produce active beam and sheet composites [20-22]. The performance of these and most other composite applications of SMA materials are heavily dependent on the quality of the SMA-matrix interface. The interface must have sufficient strength to transfer the stresses and strains from the SMA constituents to the surrounding matrix material, making the investigation of the factors affecting adhesion an important endeavor. Prior studies have investigated surface modification techniques such as sanding, sand blasting, etching, and sleeve-coupling [23-24]. However, these techniques become impractical as particle size decreases.

Our research has sought to develop an adhesion enhancing technique that can be applied to any size-scale of NiTi constituent. We have capitalized on the tools of organic chemistry to enhance adhesion. The central concept is to attach a chemical species to the well-adhering oxide of the NiTi surface [25-27] using a silane group that will be integrated into the polymerization of the matrix material, resulting in a chemical bond between the NiTi and the matrix. Silane molecules have been commonly used to bond organic materials to inorganic materials. The system studied is NiTi wires treated with various silane groups embedded in poly(methylmethacrylate) (PMMA), commonly known as Plexiglas. Testing was conducted with macroscale samples for proof-of-principle purposes.
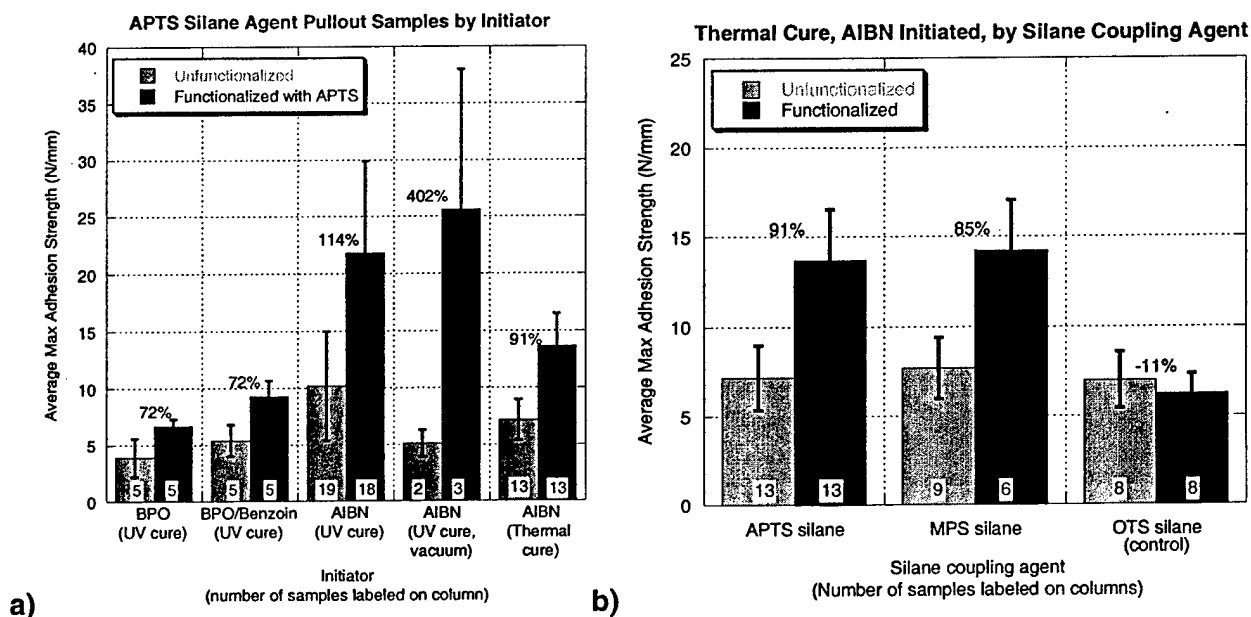
Figure 1 a) Compilation of pullout results for 3-(acryloxypropyl) trichlorosilane (APTS) surface modification under various preparation conditions involving various initiators such as Azobispropionitirile (AIBN) and various curing conditions such as UV and thermal curing. b) Different silane coupling agents are compared to control samples. APTS and 3-(Trimethoxysilyl)propyl methacrylate (MPS) contain active ends that can crosslink with the matrix monomer during polymerization, whereas the (n-octyl) trichlorosilane (OTS) is an unreactive silane control.

By varying the method of initiation and conditions of polymerization, a range of adhesion strengths can be achieved. We have shown improvement of 70% to over 100% in adhesion between PMMA and NiTi compared to unfunctionalized control samples and samples treated with an unreactive silane (OTS) lacking functionality with the monomer (Figure 1). This technique allows for adhesion control on essentially any size-scale over a range of adhesion strengths. Although the chemistry discussed here is only applicable for PMMA as a matrix material, it sets a framework for the methodology to improve the interfacial adhesion between any polymer and NiTi.

Conclusions

A range of topics was explored in our research on nanostructured shape memory alloys, particularly in reference to composite materials and components with shape memory alloy constituents. Accomplishments and new findings included the fabrication of shape memory nanoparticles, the development of a new technique for manipulating and controlling the motion of individual nanoparticles, and the demonstration of improved mechanical properties for composite applications.

We explored several fabrication and synthetic routes for the production of nanoparticles with shape memory behavior. The rolling and folding technique that we developed creates a range of particles sizes down to the nanometer scale. The chemical and electrochemical routes, although not successful in producing shape memory materials, provided fortuitous findings concerning phase stabilization in nanostructured CuSn and preliminary evidence on the feasibility of producing shape memory behavior at the nanoscale. The nanowire synthesis technique using electrodeposition was explored extensively and we were able to created patterned bristled structures as well as liberated nanowires. One of the most exciting results of our research, which has garnered substantial interest in the scientific community, was the new technique we developed for manipulating and controlling the motion of individual liberated nanowires using magnetic fields. This technique employs the use of nickel endcaps on the sample and is extremely versatile. Nickel end caps can be electrodeposited onto any conductive material in the central section of the nanowires.

In our effort to develop composite materials with shape memory alloy constituents using the nanoparticle materials discussed above, we have developed a method to improve the interfacial adhesion between the matrix and the shape memory alloy. Adhesion is a critical factor because the shape memory alloy can exhibit such large reversible strains. We demonstrated a general approach using the tools of organic chemistry that dramatically improved adhesion between NiTi and a polymeric PMMA matrix using silane functionalization. This technique is also exciting because, unlike prior methods, it can be employed on nanoscale particles.

Acknowledgements

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